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Characteristics of sol–gel deposited alumina films

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ABSTRACT

In this work, the acrylamide route has been employed for the deposition of alumina films. X-ray diffraction studies indicated the films to be amorphous for post-anneal temperatures up to 300 °C, beyond this temperature, peaks corresponding to γ-Al_2O_3 are observed. X-ray Photoelectron Spectroscopy studies show the Al 2p spectra of films. Fourier Transform Infrared spectra reveal absorption bands. The absorption coefficient was 10^4 cm^{-1}. The refractive index was found to vary in the range of 1.71–1.61 with the increase of wavelength from 250 to 500 nm.

1. Introduction

Aluminium oxide (Al_2O_3) coatings are popular for their high dielectric strength, exceptional stability, and durability against hostile environments and high transparency down to 250 nm. During the last few years Al_2O_3 coatings have been widely used for their practical applications, such as refractory coatings, antireflection coatings, anticorrosive coatings [1], microelectronic devices [2], capacitance humidity sensors [3], and also in heat sinks in IC's and passivation of metal surfaces [4], humidity sensor [5]. These films have been prepared by various techniques such as chemical vapour deposition (CVD) [6], metalorganic chemical vapour deposition (MOVCD) [7], catalytic CVD [8], spray pyrolysis [9], thermal evaporation [10], reactive sputtering [11], electrodeposition [12], anodic deposition [13], micro-arc oxidation [14], and liquid–sol method [15]. In the present work, the properties of alumina films deposited by the sol–gel technique using the acrylamide route are presented and discussed.

2. Experimental

Thin films of alumina were deposited on clean glass substrates using the following procedure. Aluminium chloride (99.99%) was dissolved in triple distilled water to form a 0.2 M solution. This solution was maintained at 70 °C and the pH of the solution was changed to 9 by adding sodium hydroxide solution. To this 0.5 g of acrylamide and 0.2 g of N,N,bis-acrylamide were added one after the other. Finally 15 mg of gelling agent ammonium persulphate was added till a viscous solution was obtained. The cleaned glass slides (2.5 cm × 7.5 cm) were inserted inside this solution and withdrawn at the rate of 0.5 cm min^{-1}. The films deposited on the surface were dried in air at 100 °C for 30 min, followed by heating at different temperatures in the range of 300–550 °C for 30 min. The films were characterized by X-ray diffraction using Phillips X-ray diffraction unit and Cu Kα radiation (1.541 Å). Optical transmission spectrum was recorded at room temperature using U 3400 Hitachi UV–vis–NIR spectrophotometer. XPS studied was carried out with VG Scientific MKII system using Mg Kα radiation (1253.6 eV).

3. Results and discussion

X-ray diffraction studies indicated that the films annealed at 300 °C are amorphous and as the annealing temperature increased from 350 to 550 °C, peaks corresponding to γ-Al_2O_3 were observed with preferential orientation in the (3 1 1) direction (Fig. 1). All peaks belonging to γ-Al_2O_3 phase are well matched with the database in JCPDS (card #41-1432). Table 1 shows the lattice spacing of the films post heat treated at different temperatures. X-ray Photoelectron Spectroscopy (XPS) studies indicated the Al 2p spectra of films after annealing at different temperatures. The films post-annealed at 550 °C exhibit a single peak with a binding energy of 74.1 eV (characteristic of Al_2O_3) while those post-annealed at lower temperatures have two peaks separated by 3 eV, which is attributed to photoemission of two separate Al_2O_3 phases present on the surface. The latter is due to the effect of different electrostatic charging during the photoemission from both Al_2O_3 phases. Similar results were reported for electrodeposited films [16]. The IR lines observed at 396.5 and 405.7 cm^{-1} are assigned to the stretching vibration of Al–O and to lattice (Fig. 2). The absorption bands in the range of 420–460 cm^{-1} are due to Al–O bonding. Some authors

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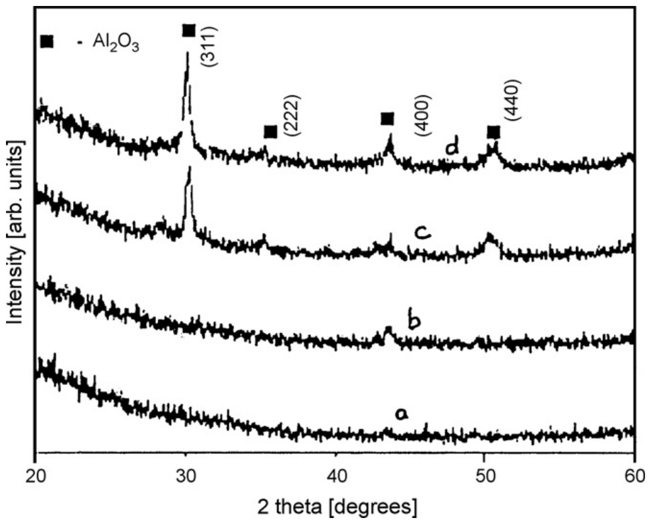

Fig. 1. XRD pattern of Al_2O_3 films post-annealed at different temperatures: (a) 300 °C, (b) 350 °C, (c) 450 °C, and (d) 550 °C.

Table 1
Lattice spacing (d) of the Al_2O_3 films post-heated at different temperatures.

h k l	d_{std} (Å)	d_{exp} (Å)		
		350 °C[a]	450 °C[a]	550 °C[a]
311	2.391	–	2.389	2.390
222	2.295	–	2.290	2.293
400	1.985	1.973	1.977	1.983
440	1.403	–	1.392	1.399

[a] Post-heat treatment temperatures.

[17] observed bands in the same spectral range for Al_2O_3 powders sintered at temperatures 600–1200 °C, which have been assigned to active and forbidden modes of α-Al_2O_3. Absorption lines located at 586 and 633 cm^{-1} are related to stretching bonding in AlO_6. The band appearing in all spectra at 668 cm^{-1} can be attributed to O–Al–O vibrations. The weak line observed at 710 cm^{-1} is due to Al–O of AlO_4 [18]. After thermal treatment at 550 °C a broad absorption band appeared at 1060 cm^{-1}. This IR band indicates the presence of Al–O–Si bond or to Al–O–Al. The IR band at 828 cm^{-1}

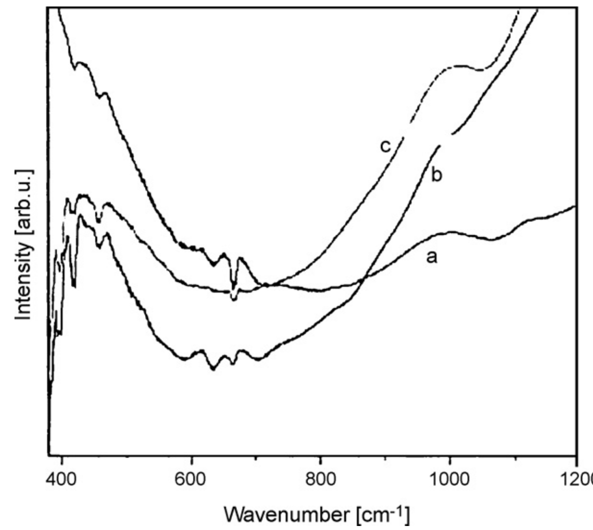

Fig. 3. FTIR spectra of Al_2O_3 films post-annealed at different temperatures: (a) 550 °C, (b) 450 °C, and (c) 350 °C.

reported by other authors [18] is assigned to crystalline aluminium oxide has not been observed in our spectra. The appearance of broad bands may be due to amorphous oxide matrix. The higher annealing temperatures lead to weakening and disappearance of the absorption bands characteristics for OH vibrations and carbon containing molecules (Fig. 3).

The optical transmittance spectra (Fig. 4) of Al_2O_3 films post-annealed at different temperatures were recorded in the wavelength range 200–850 nm. As the post-anneal temperature increased from 300 to 550 °C, the transmittance also increased from 78 to 86% at 400 nm. Higher transmittance (about 90%) at all wavelengths was observed for the films post-annealed at 550 °C. The absorption coefficient (α) was calculated from the transmission spectra. The absorption coefficient of various films was 10^4 cm^{-1}. The linear portion of the curve was extrapolated to meet energy axis at $\alpha = 0$ and the corresponding value of energy was taken as the optical band gap (Fig. 5). This was found to be in the range 5.40–5.75 eV with the increase of annealing temperature. The transmission spectra for the films post-annealed at 550 °C, exhibited interference

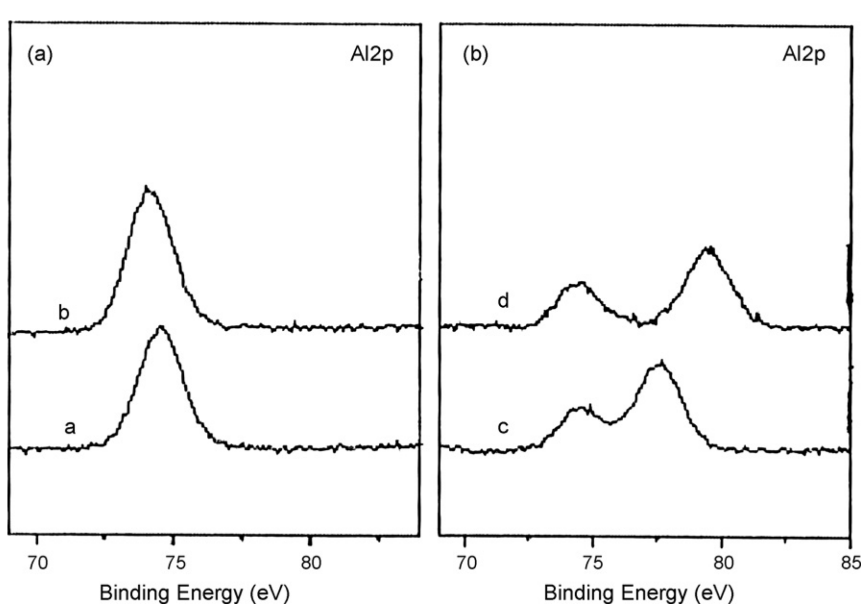

Fig. 2. XPS spectra of Al_2O_3 films post-annealed at different temperatures: (a) 550 °C, (b) 450 °C, (c) 350 °C, and (d) 300 °C.

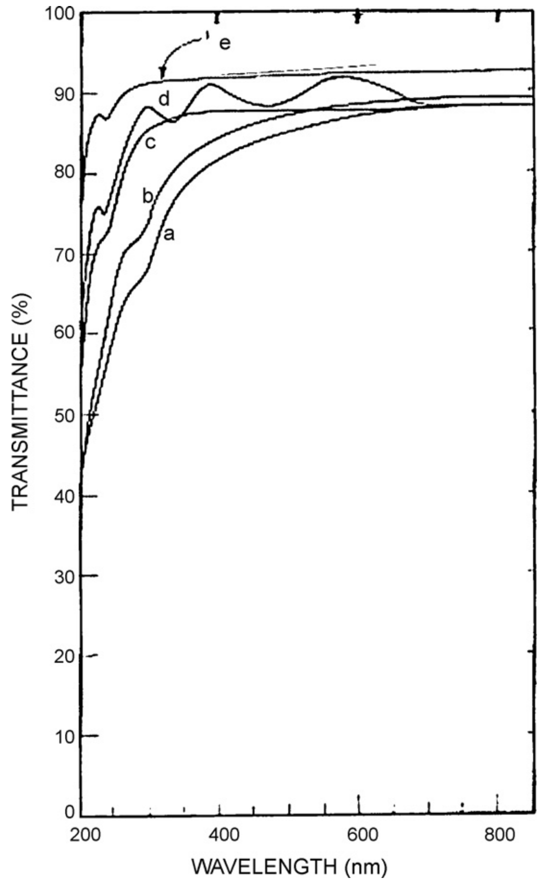

Fig. 4. Transmission spectrum of Al_2O_3 films post-annealed at different temperature: (a) 300 °C, (b) 350 °C, (c) 450 °C, (d) 550 °C, and (e) bare substrate.

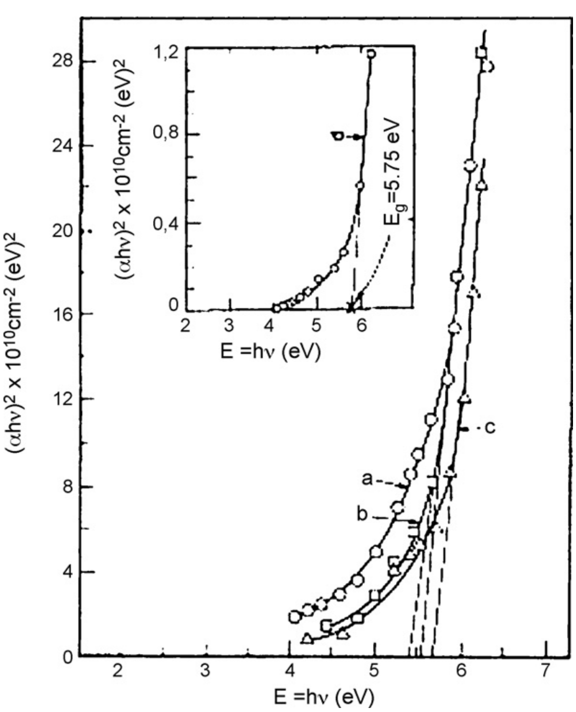

Fig. 5. $(\alpha h\nu)^2$ vs $h\nu$ plot for Al_2O_3 films deposited at different temperatures: (a) 300 °C, (b) 350 °C, (c) 450 °C, and (d) 550 °C.

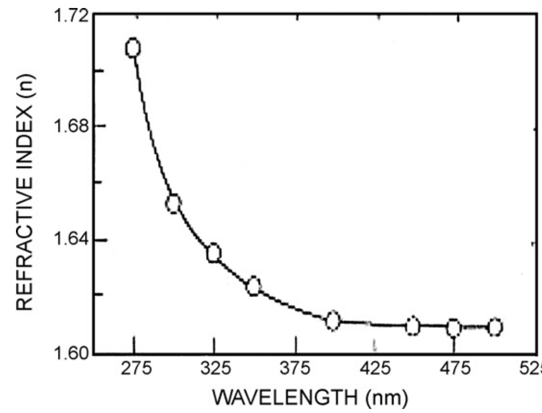

Fig. 6. Variation of refractive index with wavelength for Al_2O_3 films post-annealed at 550 °C.

fringes. The refractive index was calculated using the envelope method. It was found that the refractive index decreases with increase in wavelength and becomes almost constant at higher wavelengths beyond 400 nm (Fig. 6). These values are in good agreement with the reported values [19].

4. Conclusions

The present investigation shows that the simple and cost effective sol–gel method can be used for the formation of Al_2O_3 films. Films with high transmission in the range of 90% and with a band gap of 5.75 eV can be deposited. Single phase γ-Al_2O_3 can be obtained.

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